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Infrared and Thermal Studies of
N-(p-cyanobenzylidene)-p-oxyl-oxyaniline Coated on
Derivatized Silica"

by

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Infrared and Thermal Studies of

N-(p-Cyanobenzylidene)-p-octyloxyaniline

Coated on Derivatized Silica

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BRIEF

The interaction of the liquid crystal n - (p-cyano-
benzylidene) -p-octyloxyaniline (CBOA) with silicas modified
with monoreactive silanes varying in chain length and
blocking ability has been studied by FT-IR, DSC, and TGA.
Differences in the orientation of CBOA have been observed as
a function of derivatization.

ABSTRACT

The interaction of CBOA with silicas modified with monoreactive silanes varying in chain length and blocking ability has been studied by FT-IR, DSC, and TGA. The derivative TGA curves for the various coated silicas contain two peaks indicating the presence of a two-step desorption process. The complex shapes of the infrared nitrile stretch bands suggest three different interactions. Populations with cyano - cyano interactions, isolated nitrile groups and hydrogen bonded nitrile groups are feasible orientations. DSC data support the idea of three populations of liquid crystals with different interactions. Differences in the nitrile stretching frequencies for the octyldimethyl and decyldimethyl silicas can be explained in terms of a dynamic surface model where the bonded chains in contact with the coating reorient at a characteristic temperature and perturb the CBOA.

INTRODUCTION

Although boundary ordering mechanisms of liquid crystals are not fully understood, unquestionably it is the interfacial orientation that controls many of their display properties (1). Likewise, display failures often result from degradation of the orientation at the interface (2). In an effort to minimize this problem, more stable interfaces have been produced by modification of the substrate with reactive silanes (2).

The purpose of the current work has been to develop surface modification procedures to control the orientation of liquid crystalline molecules as well as to examine the mesogen - substrate interface. Techniques developed for related systems (i.e.,silica immobilized ligands) have been used to probe the microstructure of liquid crystals in contact with several alkylchlorosilane modified silicas. Porous silica was chosen because of its high surface area which facilitates characterization and because its surface chemistry is similar (i.e., silanol groups) to glass which is commonly used in display construction.

Previously (3) the interaction of the liquid crystal N-(p-cyanobenzylidene)-p-octyloxyaniline (CBOA) with underivatized and trimethylsilyl - derivatized silica was studied as a function of coating level. For most samples

broad asymmetrical absorption bands for the nitrile stretch suggested the presence of at least two populations of cyano groups. Subsequently, a two-site adsorption mechanism was proposed in which the nitrile groups of CBOA either formed hydrogen bonds with surface silanols or were sterically hindered from this type of interaction. Although the ratio of molecules which did not hydrogen-bond with the surface to those that did increased as the amount of the physically sorbed liquid crystal increased for both the modified and unmodified surfaces, at any given coating level, the ratio was higher for the trimethylsilane-derivatized silica than for the underivatized silica.

As a follow up to this earlier work (3), the inter-action of CBOA with silicas modified with monoreactive silanes varying in chain length and blocking ability has been studied by FT-IR, DSC, and TGA. The derivative TGA curves for the various coated silicas contain two peaks indicating the presence of a multi-step desorption process. Additionally, the complex shapes of the infrared nitrile stretch bands and the changes in the DSC thermograms DSC data support the idea of three populations of liquid crystals with different interactions.

EXPERIMENTAL SECTION

MATERIALS: The bonded phases were synthesized by refluxing Silica Gel 60 (particle size 0.040-0.063 mm, surface area $550m^2/g$ [E. Merck]) overnight in a toluene solution of a given monochlorosilane (Petrarch Systems, Inc.). During the reaction dry nitrogen was bubbled through the solution. The resulting silica was washed four times with toluene, two times with methanol, two times with ether, and then dried overnight at $110^{\circ}C$ in a vacuum oven (4). The amount of bound carbon (measured by a combustion process using a Leco 244 Carbon-Sulfur Determinator) and normalized carbon (amount of bound carbon divided by the number of carbons in the silane) for the various silicas are reported in Table 1. Subsequently, modified silicas were physically coated with between 20 and 100 w/w % CBOA. This was done by first dissolving a known amount of CBOA in ether and then adding the desired amount of silica adjusted to compensate for the weight of the immobilized silane. The mixture was allowed to equilibrate for approximately 15 minutes and the solvent slowly removed under vacuum at $38-40^{\circ}C$ with a rotary evaporator. The coated silica was dried in a vacuum oven for 43 hours at $40^{\circ}C$ and stored in a brown bottle.

SPECTROMETRY: Each undiluted sample was loaded into a 1 cm diameter diffuse reflectance cup, gently tapped to facilitate settling, and positioned in a Barnes diffuse reflectance accessory.   FT-IR spectra were collected at a resolution of 4 cm^{-1} with an IBM Instruments Model IR/32 Spectrometer equipped with a DTGS detector.   The number of sample scans needed for an adequate signal to noise ratio (i.e., 1000 to 20,000) vs. 1000 background scans were used. Baseline corrections and full scale normalizations were performed using the instrument's software.

THERMAL ANALYSIS: All thermal analysis experiments were performed in a helium atmosphere using a DuPont 9900 System for control, data collection, and data manipulation. Thermogravimetric analysis (TGA) was carried out with a DuPont 951 TGA.   Samples (8-10 mg) were conditioned at 120 10°C for 20 minutes to remove adsorbed water and then analyzed at a heating rate of 5°C /minute.   The differential scanning calorimetry (DSC) studies were made on 8-10 mg of the coated silica or 14-15 mg of the uncoated silica using a DuPont 910 DSC.   Coating weights determined by TGA were used to calculate the weight of CBOA for the coated specimens. Heating rates were 1^{O}C / minute for the coated and 10°C / minute for the uncoated samples.

RESULTS AND DISCUSSION

Surfaces were reacted with alkylmonochlorosilanes differing in chain length and blocking ability and then physically modified with from 20 to 100 w/w % CBOA. Approximately 20% CBOA has been found to correspond to a monolayer of coverage on the unmodified silica (3). This estimate will vary depending on pore geometry of the matrix (i.e., molecular exclusion effects which increase as the surface area increases), size and shape of the mesogen, and molecular alignment (5).

INFRARED STUDIES: Diffuse reflectance spectra were collected at room temperature. Shown in Figure 1 are expanded spectra from the nitrile stretching region for the various coated silicas chemically derivatized to a similar degree. Since the normalized carbon value was nearly the same for each material (i.e., 0.9 + 0.05) the relative number of unreacted surface silanols was approximately identical. In most cases broad, asymmetrical bands were observed.

The infrared spectra reflect differences in the steric accessibility of the surface silanols depending on the immobilized group. The nitrile band was severely skewed to higher frequency for butyldimethyl (Figure 1A, bands 1 and 2 for 20% and 60% CBOA respectively) and octyldimethyl (Figure

1B, bands 1 and 2 for 20% and 60% CBOA respectively) sur-
faces indicating a relatively large population of groups
which hydrogen-bond with surface silanols. For the same
coating levels on the decyldimethyl silica (Figure 1C, bands
1 and 2 for 20% and 60% CBOA respectively) the ratio of
hydrogen-bonded to non-hydrogen-bonded nitrile groups
decreased. This ratio was even lower for the more
sterically hindered tributyl surface (Figure 1D, bands 1 and
2 for 20% and 60% CBOA respectively).

The nitrile band appears to be composed of at least three
spectral components. The higher frequency component has
been assigned previously to cyano-silanol interactions (3).
The remaining two bands are especially apparent for the
decyldimethyl surface. The 20 and 60% levels are shown
respectively as band 1 and 2 in Figure 2C. As an aid in
assigning these bands, infrared spectra were collected from
CBOA dissolved in hexane, the crystalline form of CBOA, and
CBOA coated on silica highly derivatized with cyanopropyl-
dimethyl groups (9.4% bound, 1.6 normalized carbon value).
For CBOA levels of 20 and 60% on the butyldimethyl (Figure
1A, respectively bands 1 and 2) and octyldimethyl (Figure
1B, respectively bands 1 and 2) silicas, the band maxima
were at approximately the same frequency as CBOA dissolved
in hexane ($2233cm^{-1}$). The frequencies for the 20% coating on
the decyldimethyl (Figure 1C, band 1) and tributyl (Figure

1D, band 1) substrates were shifted towards the cyano-cyano frequency with the decyldimethyl band shifted more than the tributyl band.

The nitrile stretch bands for 60% CBOA coated on silica with different levels of decyldimethyl derivatization (i.e., 0.8 and 0.9 normalized carbon) are shown in Figure 2. The ratio of hydrogen-bonded to non-hydrogen bonded groups was largest on the underivatized silica (Figure 2A) and successively decreased for increasing derivatization (Figure 2B and 2C respectively).

A sample of 60% CBOA on each modified silica was heated to 120°C (i.e., above the clearing point of the liquid crystal), maintained at this temperature for 10 minutes and then allowed to cool to room temperature. Representative spectra from the nitrile stretching region for thermally conditioned samples and equivalent unheated samples are shown in Figure 3. For the underivatized surface (Figure 3A) the spectra before and after heating were nearly identical (i.e., bands 1 and 2). This was true also for the tributyl (Figure 3D) derivatized silica. Although the nitrile bands are at the same frequency for the octyl-octyldimethyl and decyldimethyl surfaces following heat treatment , this corresponds respectively to a shift to a higher and to a lower frequency for the two surface types. The nitrile frequency of the band after heat treatment was

approximately the same for all four silicas. The only differences between these bands can be attributed to differences in the ratio of molecules which hydrogen-bond to those that do not. This ratio was highest for the underivatized silica, the surface with the largest number of silanol groups and lowest for the tributyl silica, the bulkiest surface with the least sterically accessible silanols.

THERMAL STUDIES: The phase transitions for CBOA are the crystal to smectic A (73°C, 19 cal/g) the smectic A to nematic (83°C, 0.06 cal/g [6]) and the nematic to isotropic (107°C, 0.5 cal/g). The smectic A to nematic transition has been reported to be detectable by DSC only after successive recrystallizations (6,7).

DSC thermograms were collected on each surface for a series of three heating and cooling cycles. The smectic to nematic transition was not detected in any of these scans. The crystal to smectic and nematic to isotropic transitions were readily observed for coating levels of 60, 80, and 100% CBOA. The enthalpies for these changes (Table 1) correlate with the infrared data. These results reflect reasonable differences in hydrogen - bonding between the different coatings. Since the hydrogen-bonded CBOA molecules should not contribute to the transition enthalpies (5), a correlation should be possible between the transition enthalpies

and the relative population of hydrogen-bonded cyano groups for each coated silica. Enthalpy values for coated tributyl silica were the highest. Anomalously high values on the first scan for the underivatized substrate are likely due to uneven coating of CBOA during the rotary evaporation deposition process. This is supported by the observation that at the 60% level, no endothermic changes (i.e., no liquid crystalline activity) were observed for the second and third scans. After the initial scan the CBOA is believed to spread out on the surface which results in a loss of liquid crystalline properties. At the 80% coating level, liquid crystalline behavior was noted only for the decyldimethyl and tributyl silicas after a heating and cooling cycle. However at the 100% coating level, endothermic changes were observed for each silica for all scans. After a heating and cooling cycle, approximately one extra monolayer (i.e., 20%) of CBOA was required for liquid crystalline activity for the surfaces with a larger degree of hydrogen bonding. These results support the idea of puddling during the sorption process.

Besides using DSC to investigate the thermal transitions of the coated materials, TGA also was used to study the desorption of CBOA. In several cases a two-step desorption was observed. Derivative TGA thermograms for these systems can be correlated with the second and third scan transition

data measured by DSC. The single derivative peak of the TGA curve for the pure liquid crystal is shown as curve F in Figure 4. At the 100% coating level, derivative curves for the various coated silicas exhibited higher and lower temperature peaks indicating the presence of two types of desorption corresponding respectively to loss of liquid crystals from the surface at their volatilization temperature and loss at a higher temperature (i.e., a population with some interaction hindering desorption). At the 80% coating level, only the thermograms from the coated decyldimethyl and tributyl silicas (Figure 4, bands D and E) exhibited the lower temperature desorption peak. This peak was not observed at the 60% coating level. The ratio of CBOA molecules which desorb at the liquid crystal vaporization temperature to those that interact with the surface should increase with coating weight and surface derivatization and should mimic the FT-IR and DSC trends. The temperature that all of the CBOA was desorbed from each surface (i.e., the temperature the derivative curve returned to the flat baseline) is related to the degree of surface derivatization. This temperature was highest for underivatized silica and equal within experimental error for the different silicas with the same level of derivatization. Sinha and Mukherjee (8) and Harrison and Guest (9) have demonstrated differences in desorption temperature for physisorbed and hydrogen-bonded water molecules using similar TGA methods.

The differences in infrared band frequencies (Figure 3) and the lower transition enthalpies (Table 1) following a heating and

cooling cycle suggest that the CBOA molecules undergo orientational changes following heating above their clearing point. A plausible explanation for these changes is that the molecules puddle or clump on the surface during the physical coating process and spread out upon heating. Hydrogen bonding trends can be accounted for by differences in the steric accessibility of the silanols for the different derivatized silicas. However, this "puddling - spreading out" mechanism does not explain the non-hydrogen infrared band frequencies for the octyl and decyl surfaces or the frequency shifts for the heat-treated samples (Figure 3).

Both cross polarization - magic angle spinning nuclear magnetic resonance spectrometry and gas chromatography have been used to suggest a dynamic surface model where orientation and motion of the immobilized ligands are chain length dependent. The surfaces modified with longer chains behaved more like liquids while shorter chains behaved more like solids. For intermediate chains their behavior (i.e., liquid vs. solid) is temperature dependent. Thus, a possible explanation for the difference in band frequency for the CBOA coated on the octyldimethyl and decyldimethyl silica may be related to orientational changes of the immobilized ligand which occur upon heating. To judge the feasibility of this mechanism, DSC thermograms (shown in Figure 5) were collected from the uncoated octyldimethyl and decyldimethyl derivatized surfaces. For the octyldimethyl silica an endothermic transition temperature was approximately 20°C lower than for the decyldimethyl silica. The

drying temperature of the coated silicas (40°C) is respectively above and below the endothermic transition temperatures of the octyl and decyl surfaces.
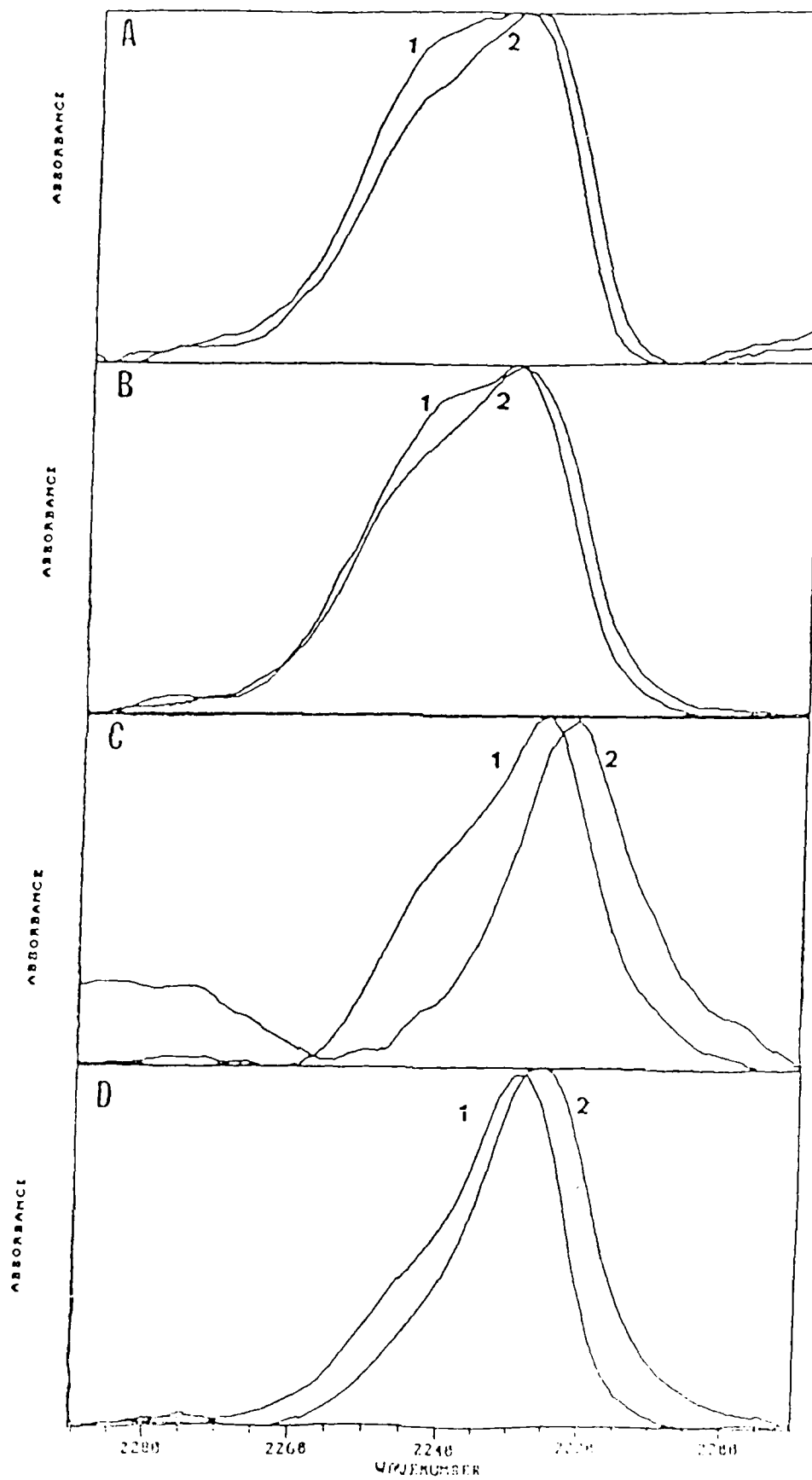
The above data demonstrate that there are differences in the orientation and interaction of CBOA with alkyl modified silicas and that these differences can be correlated to size, shape and blocking ability of the immobilized groups.
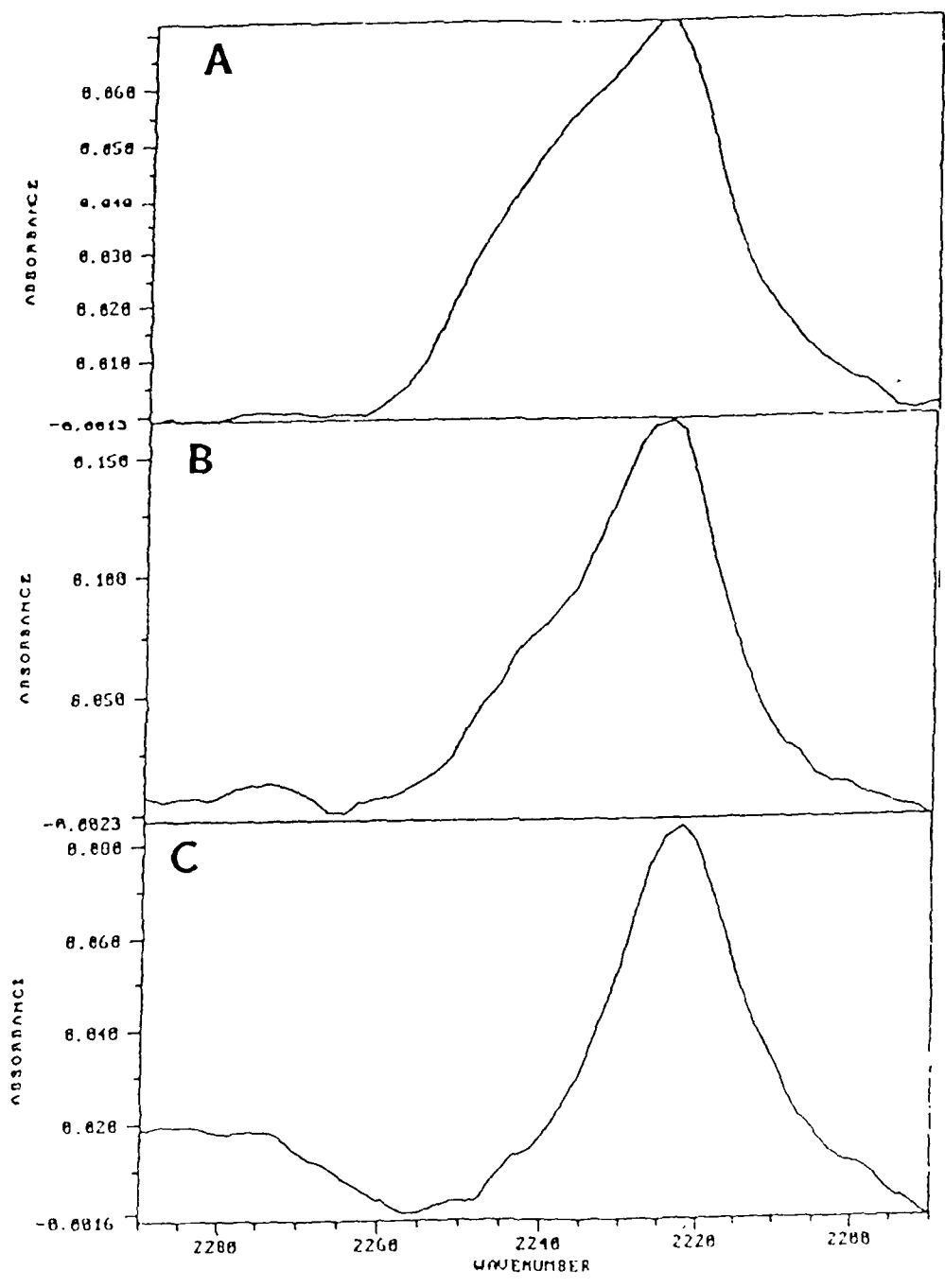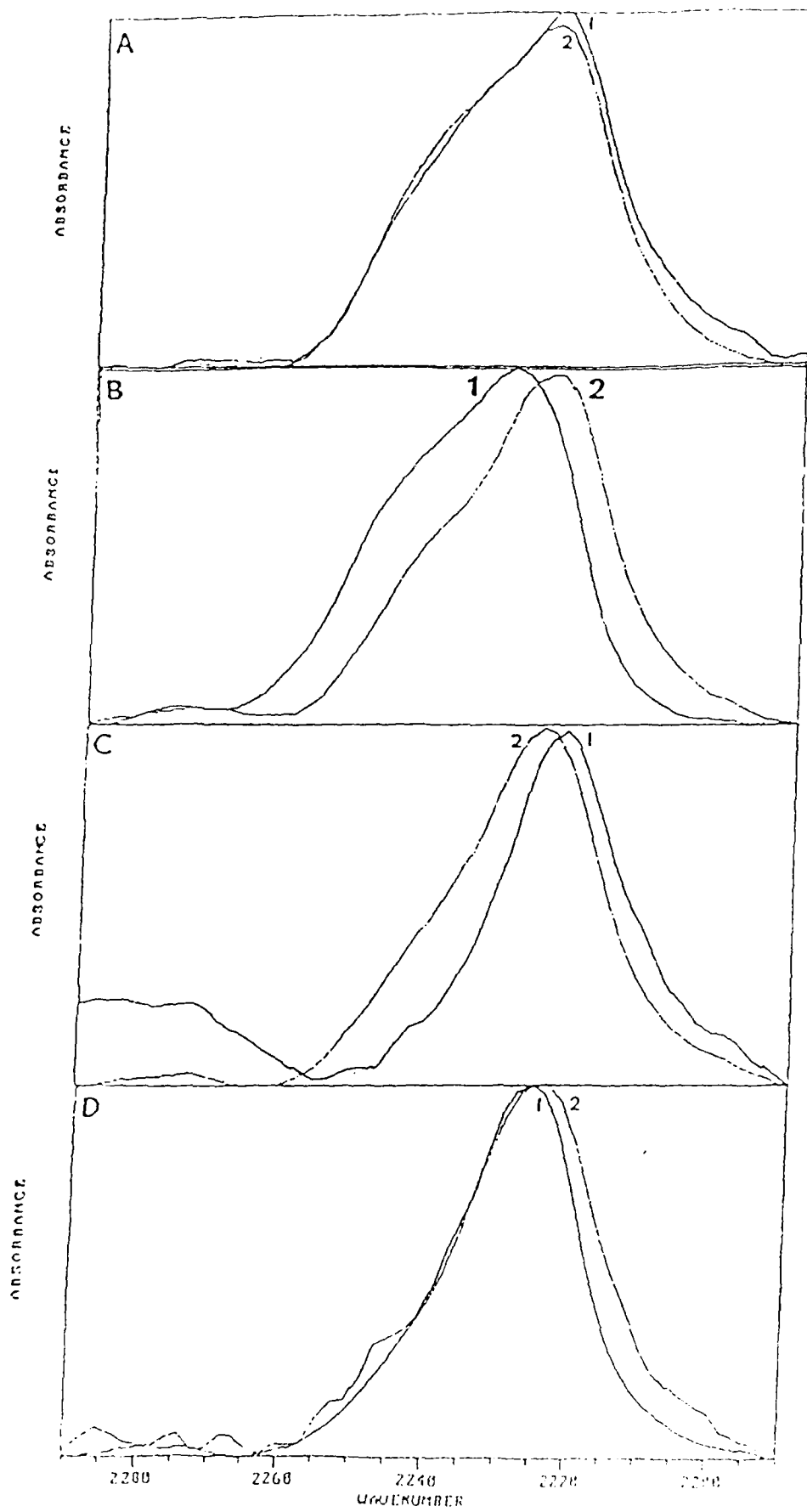
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LIST OF FIGURES

TGA

File: A: BOUNDTGA.53
Operator: CJH
Run Date: 11/13/87 13:50

Sample: 80% W/W CBOA/SILICA
Size: 12.0070 mg
Method: 5 DEG/MIN, HE ATM
Comment: A UNDERIVATIZED, B BUTYL, C OCTYL, D DECYL, E TRIBUTYL, F PURE

Deriv. Weight (%/min)

Temperature (°C)

General V2.2A DuPont 9900
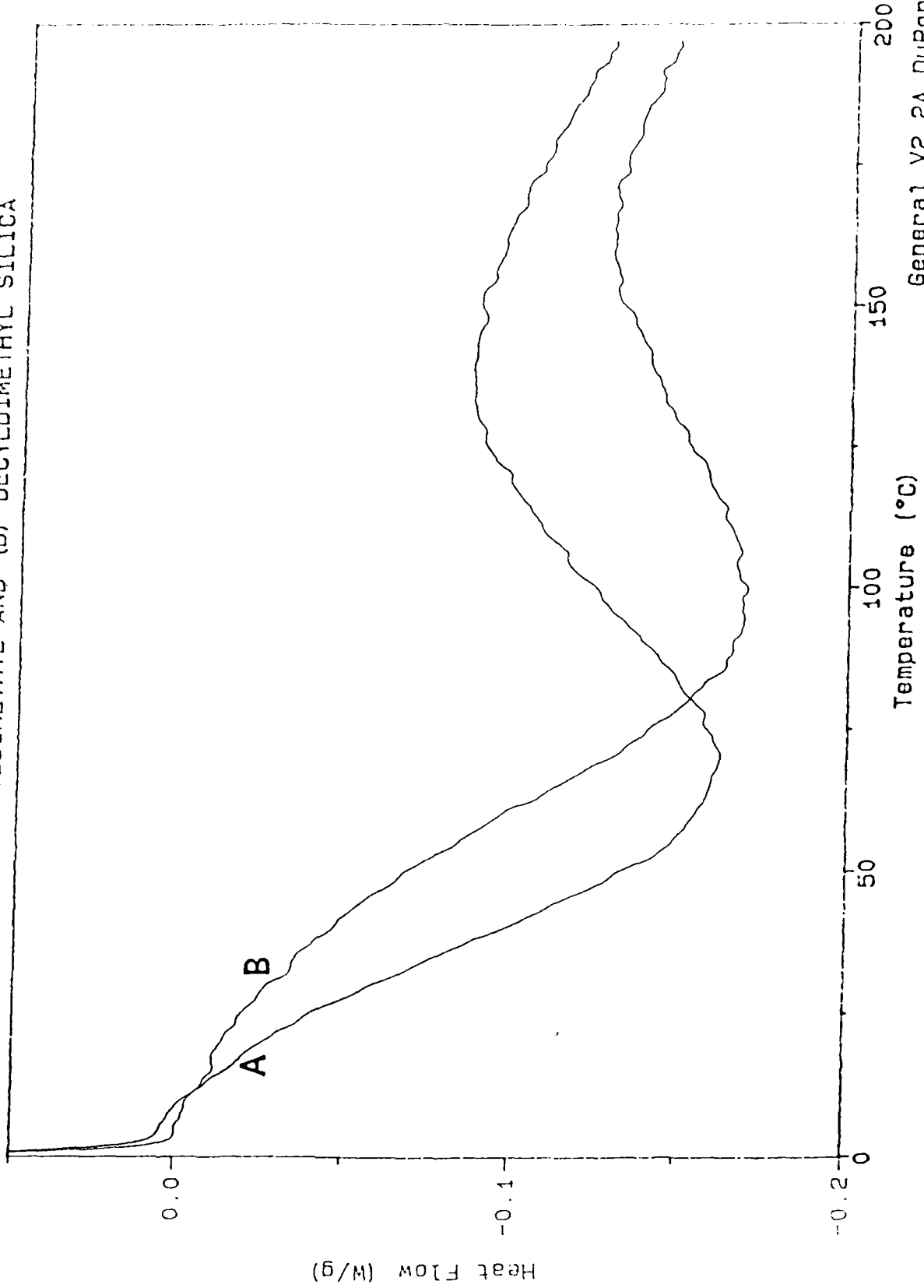
20

DSC
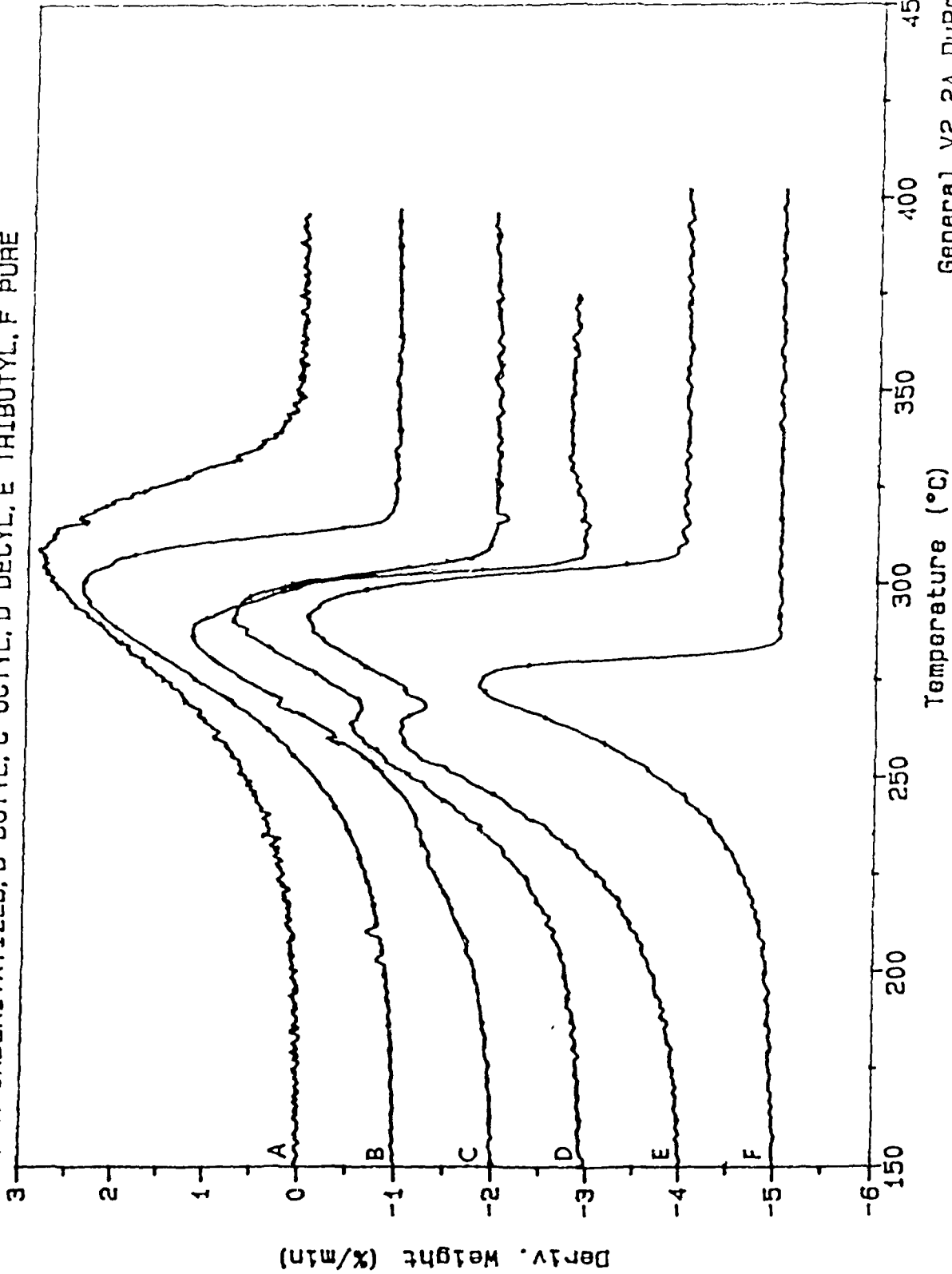
Sample: FIGURE 5
Size: 15.2300 mg
Method: DSC 10
Comment: COMPARISON OF (A) OCTYLDIMETHYL AND (B) DECYLDIMETHYL SILICA

File: A:C8DSC10.56
Operator: CJH
Run Date: 04/08/88   11:12

General V2.2A DuPont 9900

Temperature (°C)

Heat Flow (W/g)

21

TABLE 1.
ENTHALPIES (J/G) OF THE SOLID TO MESOPHASE TRANSITION FOR SILICA DERIVATIZED
WITH DIFFERENT SILYL LIGANDS AND COATED WITH VARYING AMOUNTS OF CBOA.
(% carbon-normalized carbon)   ---- no transition detected

w/w % CBOA	DSC SCAN NO.	UNDERIVATIZED (0-0)	BUTYLDIMETHYL (5.3-0.88)	OCTYLDIMETHYL (9.0-0.90)	DECYLDIMETHYL (10.8-0.90)	DECYLDIMETHYL (10.8-0.90)
100	1	14.7	24.5	18.8	17.2	35.5
	2	3.6	23.4	17.5	16.3	32.6
	3	3.4	23.2	17.3	16.2	32.6
80	1	6.3	2.5	5.4	15.9	34.3
	2	----	----	----	13.8	32.2
	3	----	----	----	13.4	32.2
60	1	2.1	1.6	0.8	4.1	4.5
	2	----	----	----	----	----
	3	----	----	----	----	----

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